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SUMMARY

An investigation was conducted to determine alloys suitable for brazing tungsten for thermal-nuclear-reactor service to 2500° C in a hydrogen atmosphere. Fifteen braze alloys with melting ranges between 2300° and 3140° C were selected and utilized for the initial melting-range and flow tests in which furnace-brazed lap joints were employed. Localized heating by gas tungsten-arc and electron beam methods were investigated, and the gas tungsten-arc method was selected for effecting straight butt-brazed joints for this study. The following 3 alloys from the original group of 15 were demonstrated to be useful in brazing tungsten base metal: tungsten - 25 weight percent osmium (W-25Os), tungsten - 50 weight percent molybdenum - 3 weight percent rhenium (W-50Mo-3Re), and molybdenum - 5 weight percent osmium (Mo-5Os). These alloys were utilized in the form of fragments (-16/+25 mesh) that were placed along a straight butt joint in 0.020-inch tungsten sheet with an initial gap of 0.010 inch. The fragments then were melted by the automatic gas tungsten-arc process in such a manner that the braze metal filled the gap by capillary flow with minimum base-metal dissolution. Eight samples were produced with each of the three selected alloys by preparing butt joints between two 0.020- by 3/4- by 3-inch pieces of tungsten sheet to produce specimens with overall dimensions of 0.020 by 3/4 by 6 inches.

These specimens were evaluated at the Lewis Research Center by nondestructive inspection, tensile tests at 2200° C (both as-brazed and after a 2500° C aging treatment in flowing hydrogen), and by metallographic techniques. On the basis of the evaluation studies, the joints brazed with the W-25Os alloy were the most suitable for high-temperature service in hydrogen. The joints brazed with the W-50Mo-3Re and the Mo-5Os alloys showed less promise under the evaluation criteria applied.

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*United Nuclear Corp., Elmsford, N.Y.

INTRODUCTION

Tungsten is of interest to NASA because of its potential usefulness in high-temperature applications, particularly in nuclear reactors (with either thermal or fast-neutron spectra) for space power and propulsion. The utilization of tungsten in high-temperature structures, however, is usually dependent on the development of suitable welding methods. One method that holds considerable potential is brazing.

The present investigation was conducted to determine suitable brazing compositions and to develop techniques for brazing tungsten for use in a thermal-nuclear-rocket reactor concept under study at Lewis. For this application, the brazing alloy is required to have a relatively low thermal-neutron-absorption cross section (it was assumed that the low-capture-cross-section isotope of tungsten (184) could be used) and that it be chemically compatible with hydrogen, the rocket propellant, at temperatures to 2500^{o} C.

A survey of the literature on the brazing of tungsten for high-temperature service yielded little applicable information. A high-temperature method of furnace brazing of tungsten was reported in reference 1. In that study, brazing was accomplished in a dry-hydrogen atmosphere at temperatures between 2200^{o} and 2825^{o} C. However, the more promising braze compositions (in weight percent) from that work (tungsten - 15 rhenium - 25 ruthenium (W-15Re-25Ru), tungsten - 35 rhodium (W-35Rh), and tungsten - 42 iridium (W-42Ir)) were not considered candidate alloys for the objectives of this study because the substantial quantities of elements (Re, Rh, and Ir) with large neutron-capture cross sections would not allow use of these braze metals in thermal-reactor applications. Several other alloys are sometimes employed in high-temperature brazing of tungsten. These alloys, in weight percent, include tungsten - 25 rhenium (W-25Re), unalloyed tantalum, and tantalum - 10 tungsten (Ta-10W). The large neutron-capture cross section of rhenium eliminated the W-25Re alloy from this study, while the tantalum compositions are unsatisfactory because of their tendency to react with hydrogen. Therefore, the brazing study reported herein was undertaken.

Within the definition of brazing, there are a number of heating processes which may be used to effect a brazed joint. These processes include furnace heating of the entire braze assembly, induction heating of the immediate area to be brazed, and localized heating by such methods as the gas tungsten-arc (TIG) process or the electron beam process. The localized heating techniques were investigated in the program to be described in this report for the following reasons:

(1) The application of heat is confined to the immediate vicinity of the joint, and thus the heat-affected region in the base metal is minimized.

(2) Work size is not limited by the relatively small, high-temperature furnaces that are available.

(3) Repair brazes may be made without heating the entire assembly.

Alloy selection and preparation and the brazing studies for this application were conducted at the United Nuclear Corporation under NASA Contract NAS 3-5205. The objective in the selection of alloys was to find compositions suitable for use with tungsten base metal in a hydrogen environment at temperatures to 2500° C. Necessary properties include good wetting action and adequate capability for capillary flow between closely fitted surfaces with minimum base-metal dissolution. Finally, the brazed joints must be free of cracks or porosity, and their strength must match the strength of the base metal at elevated temperatures. Fifteen braze alloys with melting ranges between 2300° and 3140° C were utilized for the initial melting-range and flow tests conducted on lap-joint specimens. Compositions considered included unalloyed molybdenum, seven molybdenum-base alloys, six tungsten-base alloys, and unalloyed osmium.

The best three alloys (tungsten - 25 weight percent osmium (W-25Os), tungsten - 50 weight percent molybdenum - 3 weight percent rhenium (W-50Mo-3Re), and molybdenum - 5 weight percent osmium (Mo-5Os)) and the preferred heating technique (gas tungsten-arc) were employed to prepare eight 0.020- by 3/4- by 6-inch tungsten samples for each alloy with butt joints at the 3/4- by 0.020-inch faces. These samples were evaluated at Lewis by nondestructive inspection, metallographic examination, 10-hour aging tests at 2500° C in flowing hydrogen, and tensile tests in the as-brazed and aged conditions at 2200° C in vacuum.

MATERIALS

Tungsten

Commercially pure, undoped tungsten sheet was used for this brazing program. The tungsten sheet was supplied in 3/4-inch widths and random lengths. The material was fully dense, as determined by a water displacement method and confirmed by metallographic examination. In the brazing program, the tungsten base metal was used in the as-received wrought condition. However, the gas tungsten-arc brazing operation produced a recrystallized heat-affected zone, about 0.20-inch wide, on either side of the centerline of the joint.

Braze Alloys

The following 15 alloys, whose compositions are expressed in weight percent, were selected for the screening tests:

Unalloyed molybdenum (Mo)
Molybdenum - 3 chromium (Mo-3Cr)
Molybdenum - 7 chromium (Mo-7Cr)
Molybdenum - 5 osmium (Mo-5Os)
Molybdenum - 1 palladium (Mo-1Pd)
Molybdenum - 3 vanadium (Mo-3V)
Unalloyed osmium (Os)
Tungsten - 15 chromium (W-15Cr)
Tungsten - 35 columbium (W-35Cb)
Tungsten - 50 molybdenum - 3 rhenium (W-50Mo-3Re)
Tungsten - 53 molybdenum (W-53Mo)
Tungsten - 25 osmium (W-25Os)
Tungsten - 44 osmium (W-44Os)
Tungsten - 10 ruthenium (W-10Ru)
Tungsten - 23 vanadium (W-23V)

For each alloy, 15-gram buttons were prepared by blending the material in the form of powder or chips, die pressing the material into pellets, and arc melting the pellets three times (to ensure homogeneity). Melting was performed under a partial atmosphere (~600 torr) of welding-grade argon (99.995-percent purity) with the use of the gas tungsten-arc process in a button-melting furnace. The associated vacuum system permitted evacuation to 5×10^{-5} torr before introduction of the inert gas. Before the alloys were melted, the arc was struck on a zirconium button to getter the atmosphere. The completed buttons were homogenized at 2200° C for 2 hours in helium and subsequently crushed to -16/+25 mesh fragments.

The three alloys that showed the most promise were analyzed for both major and interstitial elements. The analytical results are presented in table I.

PROCEDURE

Melting-Range and Flow Tests

In this study, a tungsten coupon 0.020 by 1/2 by 1/4 inch was placed on a second tungsten coupon 0.020 by 1/2 by 1/2 inch to form a lap joint. Braze-alloy fragments were placed at the joint, and this assembly was positioned at the bottom of a tungsten crucible (fitted with a removable lid with a tungsten-tube chimney), and the crucible, in turn, was placed in a cold wall, resistance-heated vacuum furnace. The assembly then was heated gradually under a pressure of 5×10^{-5} torr to 2200° C to assure that all surface contaminants had been evaporated. At this point, helium was admitted to

produce 1-atmosphere pressure in order to minimize loss of material by vaporization, and the temperature was raised gradually until evidence of melting was observed. The furnace was held at this temperature for approximately 30 seconds. The assembly then was allowed to cool in helium and subsequently was removed for visual and metallographic observation. The flowability of the braze alloys was evaluated on the basis of wetting action and capability for capillary flow in the lap joints.

Melting ranges for each braze alloy were observed and measured with an optical pyrometer mounted in a fixed position above the furnace window and focused on the specimen in the crucible. Since the entire crucible bottom is very similar to a blackbody, differentiation of the specimen was difficult. However, melting points were usually determined by the sudden change in emissivity on melting. Repeated measurements by different observers established that pyrometer readings could be reproducibly measured within about $\pm 10^{\circ}$ C. The pyrometer was calibrated with the furnace assembly by observing the melting points of unalloyed tantalum, molybdenum, and columbium. A curve was then constructed of observed against true melting points, and this was used to correct all observations.

Brazing Tests

The alloys that produced satisfactory lap joints in the melting-range and flow tests were evaluated by preparing straight butt joints in 0.020-inch-thick tungsten sheet with the use of either an electron beam or a gas tungsten-arc heat source. These efforts were parallel to determine which heating method was preferable.

The clamping arrangement used to hold the specimens in place during the brazing cycle is shown schematically in figure 1. Small butt joints (0.020 by 3/4 by 1 in.) were prepared with each alloy by preplacing a line of braze-metal fragments along the 3/4-inch-long joint. Early work with the electron beam heating method indicated that the clamping fixture with a heavy copper base conducted heat away from this joint so rapidly that little braze-alloy flow occurred. This problem was solved by sandwiching the tungsten coupons between glass microscope slides. The assembly was placed in a high-voltage (150 kV, 3 kW) electron beam welding chamber evacuated to 1×10^{-4} torr. Each joint was tacked at both ends by a rapid application of the electron beam prior to the principal brazing operation.

Gas tungsten-arc heating methods were applied to small butt joints in 0.020-inch-thick tungsten sheet by using an automatic setup in a chamber which was evacuated and backfilled with argon. The braze-alloy-button fragments were placed along straight butt joints with start and runoff tabs in 0.020- by 3/4- by 1-inch tungsten. A few particles of the braze alloy (-16/+25 mesh) were placed at the tab-joint intersections and

tack-brazed prior to the principal brazing operation (fig. 1). In order to minimize cracking tendency during the principal brazing operation, the holding fixtures were fully released in such a way that the joint alinement with the line of travel of the arc was not disturbed.

Preparation of Evaluation Samples

Eight straight butt joints in 0.020-inch-thick tungsten sheet were required for each of three selected braze alloys. Specimen dimensions were 3/4 by 6 inches. These specimens were made by joining two 3-inch-long coupons. Since in the brazing tests discussed later it was determined that the gas tungsten-arc heating method is preferable to the electron beam heating method, the former process was employed with a 1/16-inch-diameter, tungsten - 2-percent-thoria electrode ground to a point. Brazing was accomplished at 8 volts and 90 amperes, with straight polarity, and at a travel speed of 10 inches per minute. The operation was carried out in a welding chamber that contained less than 15 ppm oxygen and 15 ppm water vapor. The argon atmosphere was monitored for oxygen and water vapor during brazing with the use of a device described in reference 2.

The visual judgment of an adequately brazed joint was based on an even flow of alloy at the face (top) of the joint to form a crowned bead and a narrow, uniform bead at the root (bottom) side. After the brazing, it was observed that the joint gap closed considerably from the original gap set before tacking. The joint gap, which was nominally 0.010 inch before brazing, usually closed to less than 0.005 inch after brazing.

EVALUATION METHODS

Nondestructive Inspection

Radiographic and dye-penetrant inspections of the 3/4- by 6-inch brazed specimens were made at Lewis. Differences in density between braze metal and base metal, uneven distribution of braze metal along the joints, and the nature of the defects prevented meaningful results from being obtained by radiographic inspection.

Dye-penetrant inspection proved to be a useful means of detecting surface defects and subsurface defects that extended to the surface. This inspection was an especially sensitive means of detecting fine cracks in the braze metal, and it provided a bench mark for subsequent metallographic examination. This inspection operation involved the application of dye penetrant to clean surfaces, removal of the excess material with a

cleaning solution after a period of about 1/2 hour, and spraying the part with the developer, which is a chalky substance that dries on contact. The substance is stained with the dye that rises by capillary action from flaws in the surface and delineates them clearly in red.

Tensile Tests

Tensile specimens of the design shown in figure 2(a) were obtained from the 0.020- by 3/4- by 6-inch specimens in the as-brazed condition by using electrical-discharge machining procedures after most of the excess braze metal had been removed by grinding to within about 0.001 inch of the base metal. Another group of similar specimens was subject to a heat treatment in flowing hydrogen for 10 hours at 2500° C prior to machining to determine the suitability of the brazed joints for high-temperature service in a reducing atmosphere. In order to determine the tensile properties of the tungsten base metal, specimens with a shorter gage length were machined from either side of the braze in the 3/4- by 6-inch blanks as shown in figure 2(b). This procedure was necessary because no additional as-received base metal was available during the evaluation phase of this study. The gage-length region was assumed to be free of braze-heat effects; this assumption was confirmed by metallographic examination of cutouts (figs. 2(b) and 3) that revealed a typical wrought microstructure. All specimens were tensile tested at 2200° C in vacuum at a strain rate of 0.03 inch per minute. The specimens were brought to temperature with the use of a tungsten resistance heater, and the temperature measurements were obtained with tungsten - tungsten-26-percent-rhenium thermocouples. The tensile-testing apparatus is described in references 3 to 5.

Metallographic Examination

The cutouts from the tensile specimens (fig. 2) were used for metallographic examination. Sections were taken through brazed joints and unbrazed base metal to examine the microstructure. In the study of defective areas of the brazed joints, dye-penetrant indications were utilized as bench marks for obtaining metallographic specimens. In order to minimize cracking tendency during preparation, all metallographic specimens were obtained with the use of electrodischarge-machining techniques, and the specimens were mounted in an epoxy resin that was cured at room temperature. The samples then were polished by means of metallographic procedures and etched with Murakami's reagent. Microhardness determinations were employed in order to make a more comprehensive study of the microstructures. Readings were taken at room temperature with the Vickers (136°-apex, square-base pyramid) diamond indenter and a load of 500 grams.

RESULTS

Brazing Studies

Melting-range and flow tests. - A summary of the results of the melting-range and flow tests for each of the 15 alloys under consideration is presented in table II; the W-15Cr alloy was not subjected to these tests and was dropped from the program because it could not be produced in button form. All the molybdenum-braze alloys formed good lap joints on the tungsten coupons. The tungsten-base braze alloys generally showed less flow than the molybdenum-base braze alloys; however, the W-44Os braze alloy exhibited exceptionally good flow. Incomplete melting in these tests was not a criterion for alloy rejection because, in subsequent work with gas tungsten-arc or electron beam heat sources, complete melting of braze metal would be assured. Thus, the W-10Ru and the W-35Cb alloys were retained. Unalloyed osmium was dropped on the basis of severe base-metal dissolution. The 13 remaining alloys were used for brazing tests with both gas tungsten-arc and electron beam heat sources.

Brazing tests. - With the electron beam heating method, the only alloy not suitable for joining tungsten was the W-23V composition because the powder particles "blew" away in front of the beam and could not be melted in the joints. Possibly the high vapor pressure or interstitial gas content of vanadium caused the particles to move by gaseous effusion. For the other alloys, the joint cross-section geometry of electron beam brazed samples was more irregular (based on visual inspection and metallographic examination) than that which was achieved with the gas tungsten-arc process. Additionally, because of the necessity of oscillating the electron beam perpendicular to the direction of travel during brazing to fuse the braze alloy fragments, more dissolution of the base metal occurred than with the gas tungsten-arc process. If the braze alloy were preplaced in the form of wire or sheet at the joint interface, a narrower joint might be produced. However, this procedure was not attempted. Although the feasibility of brazing tungsten with the electron beam process was demonstrated, the results generally were not as promising as those obtained with the gas tungsten-arc brazing method. Thus, the gas tungsten-arc brazing method was used for the remainder of this investigation.

On the basis of a number of gas tungsten-arc brazing runs, the alloys listed in table III were dropped from the program for the reasons indicated. Alloys that still showed good promise were as follows: Mo-3V, Mo-5Os, Mo-1Pd, W-50Mo-3Re, W-23V, W-25Os, and W-35Cb.

Hydrogen heat-treatment effects. - The number of alloys still under consideration was further reduced when it was observed that heat treatment at 2200^{o} C in hydrogen for 2 hours followed by cooling in hydrogen produced porosity in the W-35Cb and W-23V alloys. The Mo-3V alloy also was dropped from the program because of the possibility

that the vanadium might react with hydrogen over longer periods of time. In addition, the Mo-1Pd alloy was eliminated because over a period of time the palladium might evaporate. Thus, only the following alloys were available after the screening tests were completed: W-25Os, W-50Mo-3Re, and Mo-5Os. For the final evaluation, eight specimens (0.020 by 3/4 by 6 in.) were butt brazed with each of these three alloys.

Nondestructive Inspection

The results of the dye-penetrant inspection of the specimens brazed with the final three alloys are shown in table IV. Arc-start and crater defects were not included in the tabulation because their extent and frequency reflected the specific conditions and procedure used for each run. Also, the start and crater areas were generally located on arc-starting and runoff tabs. Photographs of a typical brazed joint are shown in figure 4. It should be noted that at the root the braze metal is quite narrow compared with the amount of material that is present at the face of the joint. The braze-metal cracking that was observed along the joint for the Mo-5Os and W-50Mo-3Re alloys tended to be randomly oriented and was located primarily at the face of the joints. However, cracks observed in the W-25Os braze metal were unique in regard to the pattern. These cracks, which were almost exclusively confined to the root of the joint, were present in the form of uniformly spaced hairline cracks in the braze metal, transverse to the joint.

Tensile Tests

Tensile data for specimens which were machined transverse to the brazed joints (fig. 2(a)) are presented in table V. The engineering stress at fracture was computed for both the braze metal and the tungsten base metal because the section thickness at the brazed joint was slightly greater than that of the balance of the specimen. For joints brazed with the W-25Os alloy, fracture was located in the base metal in both the as-brazed and heat-treated conditions. The as-brazed W-50Mo-3Re specimen 414 failed outside the joint, but in a similar specimen (412) in the heat-treated condition, fracture took place partly in the braze metal and partly in the base metal. In the as-brazed condition, fracture took place in the braze metal for the Mo-5Os alloy (418) at a relatively low stress of 2330 pounds per square inch. Metallographic examination of a cutout machined from the tensile blank revealed the presence of intergranular cracking in the braze metal. This defect probably led to the premature failure that was obtained. In

the heat-treated condition, fracture occurred outside the Mo-5Os braze metal (398), and the associated fracture stress was similar to those obtained with the other alloys.

Average strength of the tungsten base metal, as judged from the specimens that failed 1/8 to 3/8 inch from the braze metal, was of the order of 3000 pounds per square inch for both as-brazed and heat-treated specimens. Tensile tests of five tungsten base-metal samples (fig. 2(b)) revealed strength values that varied from 2820 to 5080 pounds per square inch. The average strength, 3900 pounds per square inch, is comparable to the ultimate tensile strength of a low-strength lot of wrought-sintered tungsten sheet (ref. 3). The reason for the wide variation in strength is not known. Thus, although the average strength of the tungsten base metal was greater than that of the specimens with a brazed joint, the strength of the brazed specimens generally fell within the scatter band for the strength of the tungsten.

Metallographic Examination

Brazed specimens. - Cross sections of as-brazed joints obtained from the tensile-specimen cutouts are presented in figures 5 and 6. The microstructure of the joint in figure 5 illustrates a completely recrystallized base-metal heat-affected zone (compared with that shown in figure 3 for as-received tungsten base metal) and the $\alpha + \sigma$ phase structure characteristic of the W-25Os alloy (ref. 6). Some scattered braze-metal porosity may also be seen in figure 5. The gap between the mating surfaces of the joint is about 0.010 inch, and it is evident in this case that the edges of the tungsten base metal were partly dissolved in the braze metal. A case of extreme base-metal grain growth is also evident on the left side of the joint shown in figure 5. The single-phase microstructure of the W-50Mo-3Re alloy, shown in figure 6, also is representative of the Mo-5Os braze metal. For this joint the braze metal fills a gap about 0.005 inch wide.

Cross sections taken from joints tensile tested at 2200° C (figs. 7 and 8) show little change in appearance from as-brazed specimens. In the joint shown in figure 7, the braze metal flowed into a gap 0.0005 inch wide. For the tensile specimens shown in figures 7 and 8, failure occurred in the base metal 1/8 and 3/16 inch, respectively, from the edge of the braze metal. A photomicrograph of the base-metal failure (fig. 9) in a specimen brazed with the W-25Os alloy (385) shows a knife-edge fracture surface with a wedge-shaped single grain believed to be strain induced.

Photomicrographs of brazed joints subjected to heat treating in hydrogen for 10 hours at 2500° C are shown in figure 10. For the W-25Os braze alloy, little evidence of the braze alloy remains at the joint (fig. 10(a)) except for a two-phase region of the face (top) of the joint. No detrimental effects were observed with this braze alloy except for a few widely scattered pores. Substantial porosity is evident in the other two braze metals

(W-50Mo-3Re and Mo-5Os) along with some loss of braze metal at the outer surfaces. The internal porosity is believed to be due to the Kirkendall diffusion effect, while the loss of material at the surface is most likely due to vaporization of the molybdenum. Vaporization is more pronounced in the Mo-5Os alloy (fig. 10(c)) than in the less molybdenum-rich W-50Mo-3Re composition (fig. 10(b)). However, despite the observed porosity and loss of material at the surface, the Mo-5Os tensile specimen (398 in table V) failed in the base metal.

Microhardness determinations. - Microhardness values for the brazed joints are summarized in table VI. In the as-brazed condition the W-25Os braze metal was extremely hard (1100 kg/mm^2) compared with the tungsten base metal (360 kg/mm^2). The W-50Mo-3Re alloy (220 kg/mm^2) and the Mo-5Os alloy (290 kg/mm^2) were softer than the tungsten base metal in the as-brazed condition. After heat treatment (10 hr at 2500° C in hydrogen), the W-25Os alloy was much softer (385, 480, and 680 kg/mm^2) in α-phase regions. Hard spots (1270 kg/mm^2), however, were still found in regions where the σ phase was present (fig. 10(a) and table VI). Because of the tendency for scatter in the high-hardness range and because the hardness value of 1270 kilograms per square millimeter is from a single determination, it is felt that heat treatment did not increase the hardness in the $\alpha + \sigma$ region from 1100 to 1270 kilograms per square millimeter, but rather the hardness is probably similar to that determined in the as-brazed condition. On the other hand, the variation in hardness (385 to 680 kg/mm^2) in the α-phase regions of the heat-treated W-25Os alloy is believed to be the result of an osmium-composition gradient; that is, the richer the α phase is in osmium, the greater is the hardness. Hardness determinations on the tungsten base metal and the other two braze metals revealed that there was essentially no change in hardness due to the heat treatment.

Braze-metal cracking. - A photomicrograph illustrating the intergranular nature of the cracking which was observed in the W-50Mo-3Re alloy is shown in figure 11. This condition was probably hot cracking that occurred as a result of the presence of a film of oxide at the grain boundaries. Cracking of this type was also observed in the Mo-5Os alloy.

A high-magnification photomicrograph that illustrates another type of cracking encountered in the W-25Os alloy is presented in figure 12. This condition is believed to be cold cracking that occurred after the joint had cooled from the brazing heat but was still considerably above room temperature. Close examination (fig. 12) revealed that the cracking followed the σ phase, the interface between α and σ phases, and the ribs within the α dendrites which are probably rich in σ phase. The cracking did not progress into the bulk of the α dendrites.

Tungsten base metal. - Metallographic examination was conducted on the tungsten tensile specimens tested in order to determine whether there was a marked difference in structure between the tensile specimens with the highest (5080 psi) and lowest (2820 psi)

strength. Photomicrographs of these specimens, shown in figure 13, illustrate the marked difference in grain size after tensile testing. As would be expected from published data (refs. 3 and 7), the strength obtained can be correlated with the grain sizes as determined after testing; that is, the larger grain size material was weaker. However, the reasons for the difference in grain size from specimen to specimen are not known. Another observation regarding grain size was the nonuniform grain growth within a single tensile specimen, as shown in figure 13(c). The microstructure of both the high- and low-strength specimens prior to testing was similar to that shown in figure 3.

DISCUSSION

All factors considered, the W-25Os composition appears to hold the greatest promise as a braze metal for tungsten for nuclear service to 2500° C in a hydrogen environment. The high-temperature tensile strength of the W-25Os is good in view of the fact that failure occurred in the base metal for two transverse tensile tests at 2200° C. No significant Kirkendall porosity or other detrimental effects were observed as a result of a 10-hour heat treatment at 2500° C in flowing hydrogen. In fact, this braze metal may be improved by heat treatment in that the σ phase tends to be transformed to the α phase, which produces a substantial reduction in braze-metal hardness. The tensile data were clouded somewhat by the fact that the specific lot of tungsten base metal exhibited a wide and relatively low range of tensile-strength values at 2200° C. For this reason, the braze metal may not have been tested as severely as it would have been if a stronger base metal had been employed. The W-50Mo-3Re and Mo-5Os braze metals were less promising than the W-25Os composition because Kirkendall porosity and evaporation developed from the 2500° C heat treatment.

In regard to cracking tendency, the W-25Os alloy was sensitive to cold cracking, that is, cracking which develops below the solidification temperature in the σ phase. This type of cracking can usually be avoided by minimizing restraint and optimizing brazing parameters. The uniformly spaced, transverse, hairline root cracks, which were observed in the evaluation specimens, probably could have been avoided if more braze metal were present at this location.

The randomly oriented cracking encountered in the W-50Mo-3Re and Mo-5Os alloys is more difficult to combat since it is an intergranular hot-cracking phenomenon. The reason for this difficulty is believed to be associated with the fact that molybdenum has extremely low oxygen solubility (about 1 ppm), and thus oxide phases are always present (ref. 8). The oxygen reacts to form a molybdenum - molybdenum oxide eutectic that segregates to the grain boundaries. Probably this or some other more complex eutectic

in the form of a thin film remains molten for a sufficient period of time so that a situation results wherein shrinkage stresses are applied normal to a molten grain boundary with resultant intergranular tearing.

CONCLUDING REMARKS

The brazing development program described in this report resulted in the selection of three alloys (W-25Os, W-50Mo-3Re, and Mo-5Os) and one heating method (gas tungsten-arc) for preparation of the evaluation specimens. In regard to the screening tests for the braze alloys, this test program was not exhaustive, and some alloys may have been dropped from the program in an arbitrary manner. This procedure was necessary, however, because of economic considerations. A certain number of the alloys that showed good promise in the early work involving furnace-brazed lap joints (table II) may be well worth investigating further, particularly for furnace-brazing applications. In regard to further development of any of these braze-alloy compositions, it would be highly desirable to produce the braze metal in the form of wire or sheet to aid placement of the alloys in the joint regions.

Further optimization of gas tungsten-arc procedures and/or the development of other heating sources, such as plasma arc or low-voltage (30 kV or less) electron beam, may offer improved methods of localized heating of joints for the brazing operation.

In view of the high cost and rareness of osmium, it would be desirable to utilize the smallest possible amount of this material. Another reason to reduce the osmium content would be to minimize or eliminate the σ phase in the very promising W-25Os alloy. Therefore, if future efforts are undertaken with alloys of this general type, it may be well worthwhile to study the 10- to 20-weight-percent-osmium range with additions of other elements to reduce the melting point of the alloy.

When working with osmium, care must be taken to avoid the inhalation of noxious osmium tetroxide fumes. In the brazing program described in this report, essentially no osmium tetroxide fumes are believed to have been formed since alloy-button melting took place in an inert atmosphere and brazing was conducted in either an inert-gas atmosphere or a vacuum environment.

SUMMARY OF RESULTS

A group of 15 alloys was studied and evaluated for use as braze materials for tungsten base metal in nuclear applications for service in a hydrogen atmosphere at temperatures to 2500^{o} C. Brazed butt joints were prepared with the three most promising

braze alloys. These joints were evaluated by nondestructive inspection, metallographic examination, heat treatment at 2500° C in hydrogen, and tensile tests at 2200° C. The principal results of the evaluation were as follows:

1. Gas tungsten-arc brazing procedures were successfully applied to produce fully brazed, crack-free joints in tungsten which meet the strength and serviceability requirements for high-temperature nuclear service in hydrogen.

2. The most promising of the 15 alloys studied was the tungsten - 25-weight-percent-osmium (W-25Os) composition. Tensile failures were located in the base metal in both the as-brazed and heat-treated conditions, and no significant Kirkendall voids or loss of material due to vaporization occurred during heat treatment. Other promising alloys were the tungsten - 50-weight-percent-molybdenum - 3-weight-percent-rhenium (W-50Mo-3Re) and the molybdenum - 5-weight-percent-osmium (Mo-5Os) compositions.

3. Cracking to some extent was observed for each braze metal. For the W-25Os alloy the problem seemed to be a less severe, cold cracking, but for the W-50Mo-3Re and Mo-5Os alloys there appeared to be a more difficult-to-combat, intergranular, hot-cracking problem.

4. A high-voltage electron beam heating method was shown to be feasible for use in brazing tungsten, but it was less promising than the gas tungsten-arc approach.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, January 31, 1967,
122-28-01-01-22.

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TABLE I. - CHEMICAL COMPOSITION OF BRAZE ALLOYS

Braze alloy	Major elements, wt %				Interstitial impurities, ppm		
	W	Mo	Os	Re	C	O	N
W-25Os	Bal.	---	24.3	---	53	104	36
			24.6		59	201	52
W-50Mo-3Re	Bal.	49.5	----	3.1	22	102	10
					51	114	51
Mo-5Os	---	Bal.	4.4	---	27	115	16
			4.7		48	139	50

TABLE II. - BRAZE-ALLOY COMPOSITION, MELTING RANGE, AND EVALUATION

Nominal alloy composition, wt %	Melting range, °C		Results of visual and metallographic evaluation of furnace-heated lap-joint assemblies
	Predicted (a)	Observed (b)	
Mo (unalloyed)	2620 (ref. 6)	2605	Good flow, no erosion
Mo-3Cr	2590 to 2600 (ref. 6)	2605 to 2695	Good flow, no erosion
Mo-7Cr	2540 to 2570 (ref. 6)	2500 to 2530	Good flow, no erosion
Mo-3V	2500 to 2610 (ref. 9)	2605 to ?	Excellent flow, very fluid, no erosion
Mo-5Os	2550 to 2570 (ref. 9)	2595 to ?	Good flow, no erosion
Mo-1Pd	2520 to 2590 (ref. 6)	2630 to ?	Good flow, no erosion
W-53Mo	2970 to 3000 (ref. 6)	2930 to ?	Moderate flow, no erosion
W-50Mo-3Re	----------	2855 to ?	Fully melted, fair flow, no erosion
W-23V	2300 to 2620 (ref. 9)	2945 to 3025	Moderate flow, no erosion
W-25Os	2930 to 3060 (ref. 6)	2975 to ?	Moderate flow, no erosion, residue left outside joint
W-44Os	2710 to 2740 (ref. 6)	2675	Good flow, no erosion
W-35Cb	2975 to 3140 (ref. 6)	2940 to ?	Poor flow, did not melt completely, no erosion
W-10Ru	[c]2975 (ref. 6)	3055 to ?	Partial melting, no flow, no erosion
Os(unalloyed)[d]	2980 (ref. 9) 2700 (ref. 10)	2695	Excellent flow, severe erosion, dissolves base metal
W-15Cr[d]	----------	None	Could not produce alloy button

[a]Solidus-liquidus from equilibrium phase diagrams in the references cited.

[b]First number is the initiation of observed melting; second number is the temperature at which the alloy flowed readily. The question mark indicates that full liquidation was not observed.

[c]Liquidus temperature not available.

[d]Alloys dropped from program prior to brazing tests.

TABLE III. - ALLOYS ELIMINATED ON BASIS OF GAS TUNGSTEN-ARC BRAZING TESTS

Alloy composition, wt %	Reason for elimination
Mo (unalloyed)	Only fair flow
Mo-3Cr Mo-7Cr	Severe base-metal erosion
W-53Mo W-10Ru W-44Os	Braze-metal cracking

TABLE IV. - RESULTS OF DYE-PENETRANT INSPECTION

Braze-alloy composition, wt %	Number of specimens examined	Number of crack-free specimens	Number of specimens containing braze-metal cracks
Mo-5Os	8	5	3
W-50Mo-3Re	8	5	3
W-25Os	8	4	4

TABLE V. - RESULTS OF TENSILE TESTS AT 2200° C

Specimen number	Braze-alloy composition, wt %	Condition (a)	Engineering stress at fracture, psi		Location of fracture (b)
			Base metal	Braze metal	
385	W-25Os	AB	3060	2620	Base metal, 1/8 in. from braze metal
395	W-25Os	HT	2810	2610	Base metal, 1/8 in. from braze metal
414	W-50Mo-3Re	AB	2930	2610	Base metal, 3/16 in. from braze metal
412	W-50Mo-3Re	HT	3110	2820	Partly base, and partly braze metal
418	Mo-5Os	AB	2770	2330	Braze metal
398	Mo-5Os	HT	2960	2630	Base metal, 3/8 in. from braze metal

[a]AB, as brazed;
HT, heat treated at 2500° C for 10 hr in hydrogen.
[b]Distances from braze metal at face of joint.

TABLE VI. - VICKERS MICROHARDNESS DETERMINATIONS

[Load, 500 g; values stated in kg/mm^2.]

Material (alloy compositions stated in wt %)	As-brazed condition	Heat-treated condition (a)
W-25Os braze metal	[b]1100 ($\alpha + \sigma$)	385, 480, 680 (α region) 1270 ($\alpha + \sigma$)
W-50Mo-3Re braze metal	[b]220	240
Mo-5Os braze metal	[b]290	[c]280
Tungsten base metal	[d]360	[b]355

[a]Heat treated at 2500° C for 10 hr in hydrogen.
[b]Average of three determinations.
[c]Average of two determinations.
[d]Average of eight determinations.

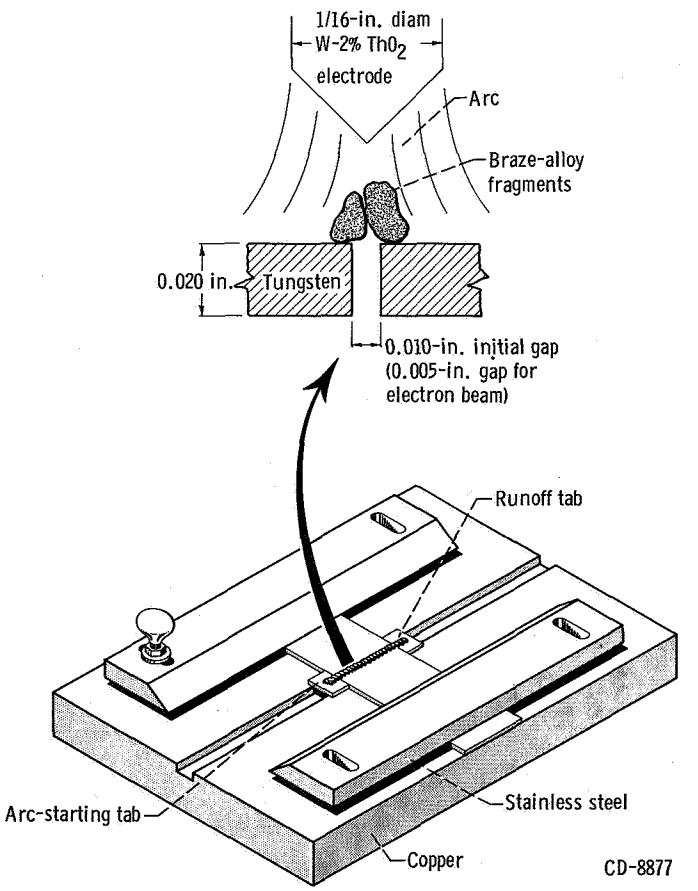
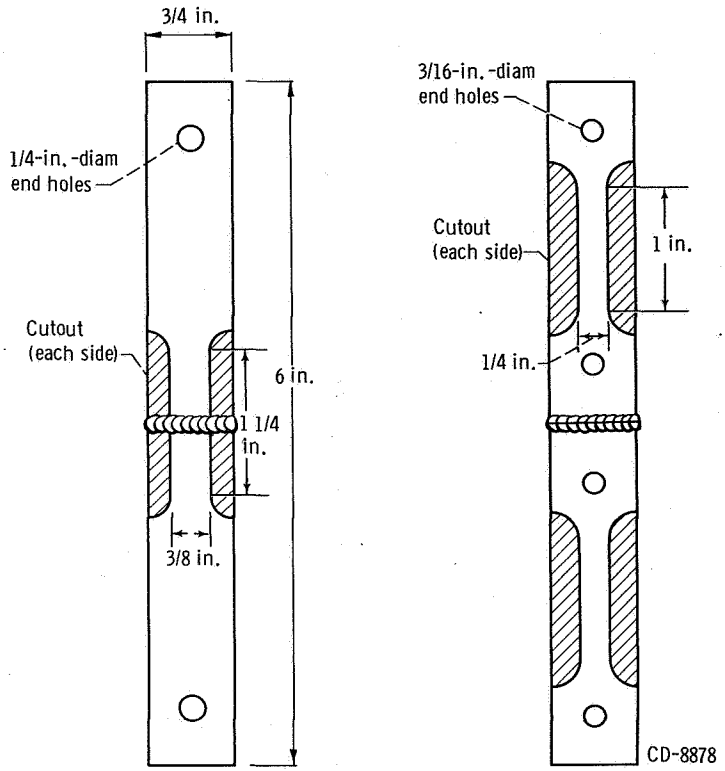


Figure 1. - Clamping arrangement used to hold specimens in position during brazing. (An electron beam may be used in place of the arc.)



(a) Brazed tensile. (b) Base metal tensile.

Figure 2. - Tensile specimens in 0.020-inch brazed tungsten sheet.

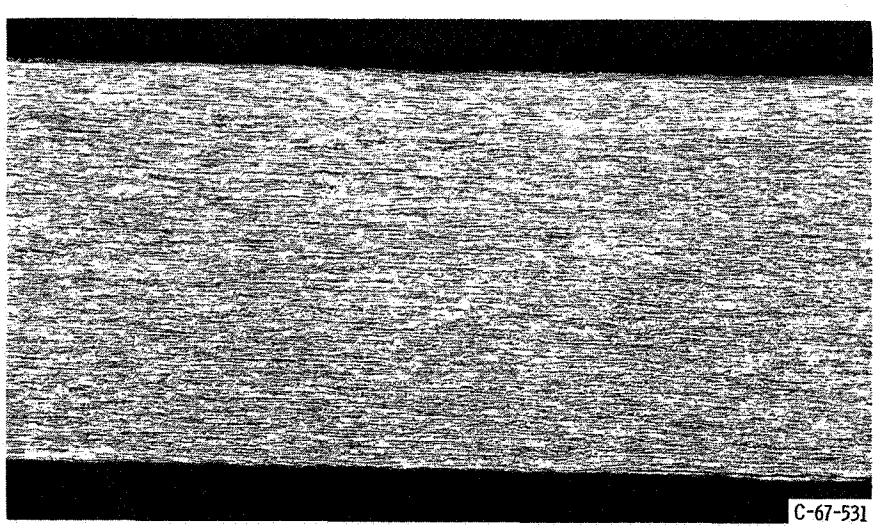
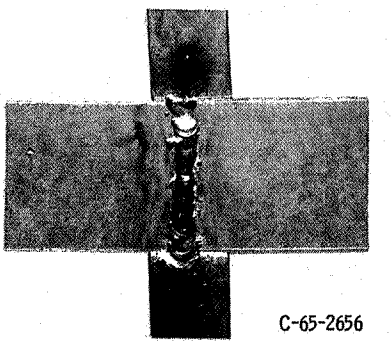
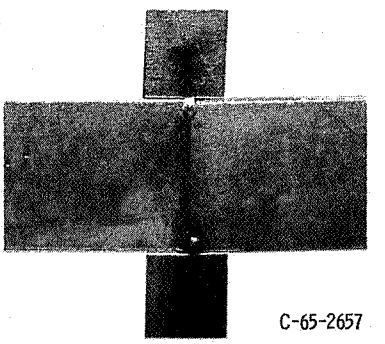


Figure 3. - Microstructure of tungsten sheet in wrought, as-received condition. This cross section was obtained from sample cutout from base-metal tensile specimen (fig. 2(b)). Etchant, Murakami's reagent. X100.



C-65-2656

Face

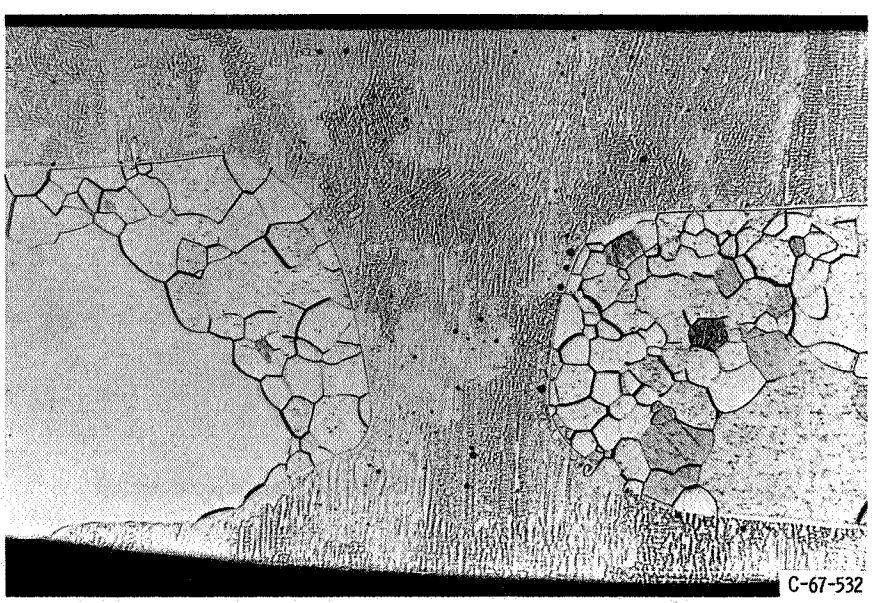


C-65-2657

Root

Figure 4. - Tungsten specimen brazed with tungsten - 25-weight-percent-osmium alloy.

←0.010-in. gap→



C-67-532

Figure 5. - As-brazed structure of two-phase, tungsten - 25-weight-percent-osmium alloy and recrystallized tungsten base metal. Section obtained from cutout from tensile blank. Etchant, Murakami's reagent. X100.

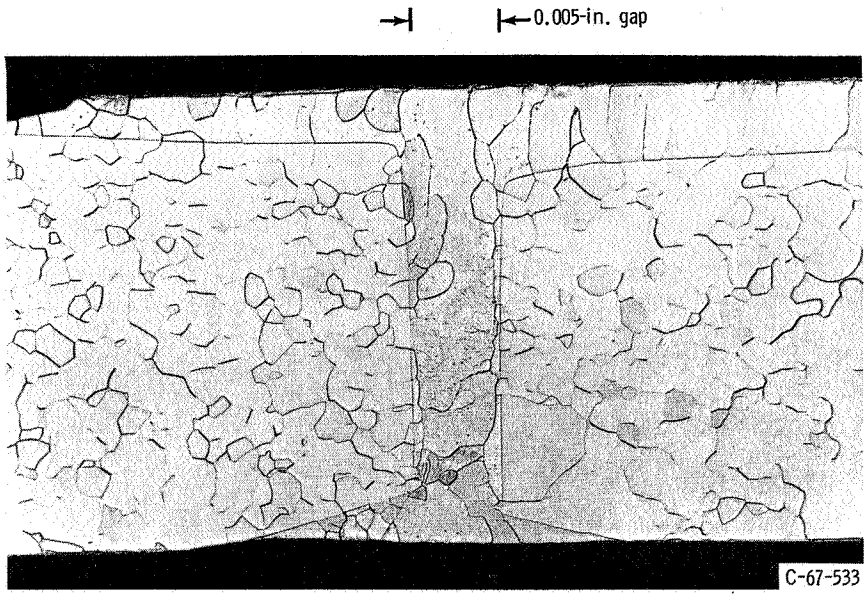


Figure 6. - As-brazed joint in tungsten base metal produced with single-phase, tungsten - 50-weight-percent-molybdenum - 3-weight-percent-rhenium alloy. Section obtained from cutout of tensile blank. Etchant, Murakami's reagent. X100.

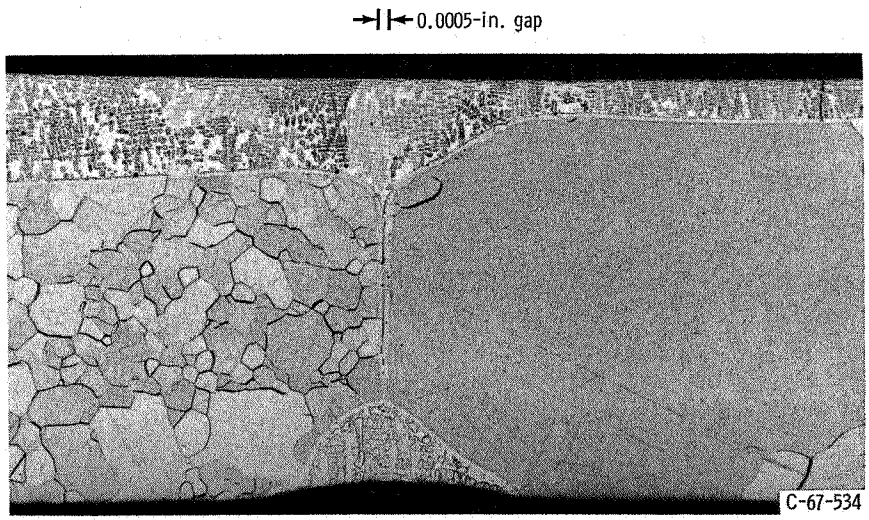


Figure 7. - Cross section of tested tensile specimen 385. Face (top) of joint has been ground flat; tungsten base metal is reduced in thickness at left side of joint because of erosion; dissolution effect is also evident at root (bottom) of joint; braze alloy, tungsten - 25-weight-percent-osmium. Etchant, Murakami's reagent. X100.

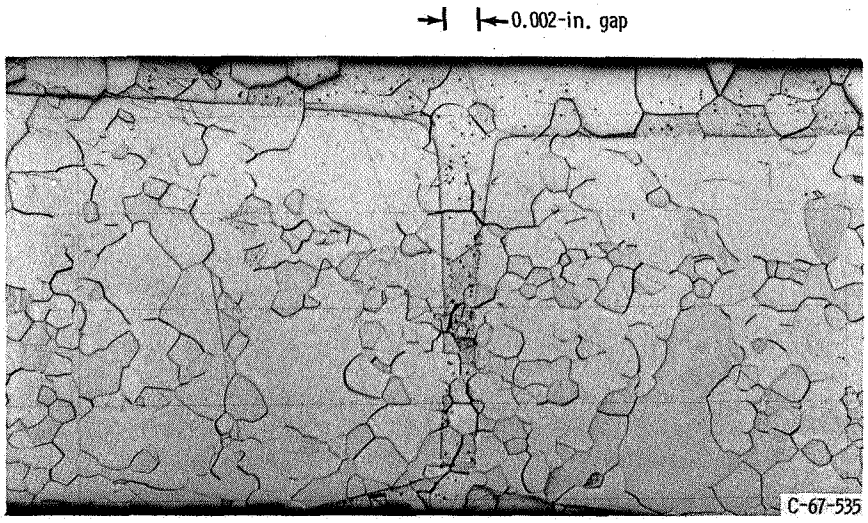


Figure 8. - Cross section of tested tensile specimen 414. Epitaxial growth of braze-metal grains is evident at interface between tungsten base metal and braze metal; dissolution effects may be noted at face on right side of joint and at root of joint; braze alloy, tungsten - 50-weight-percent-molybdenum - 3-weight-percent-rhenium. Etchant, Murakami's reagent. X100.

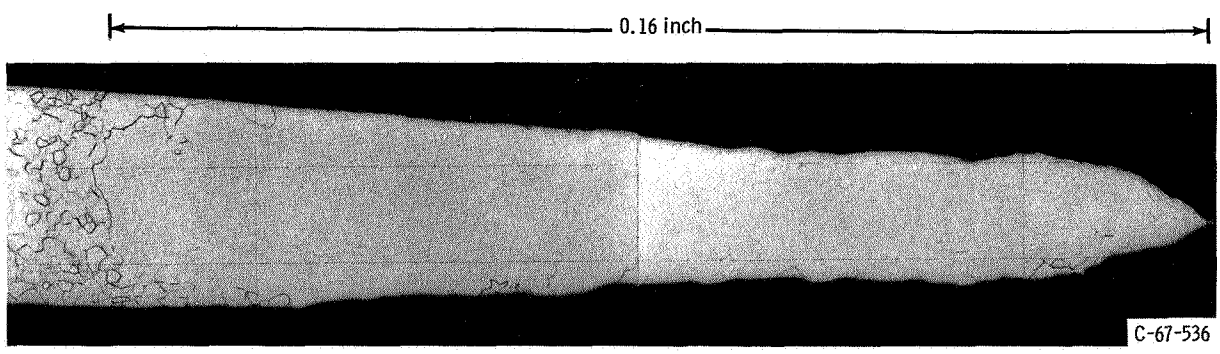
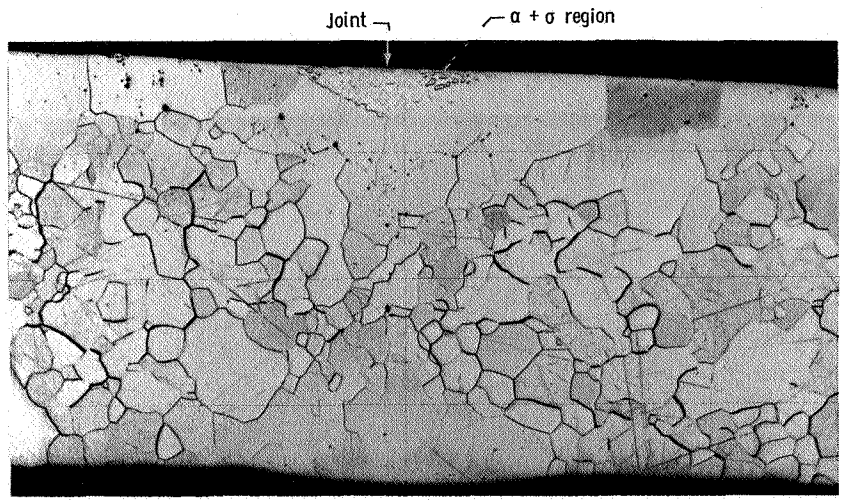
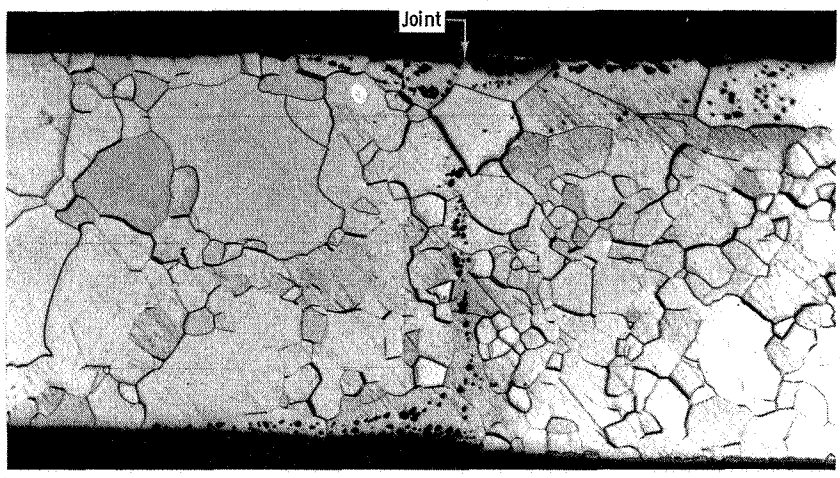


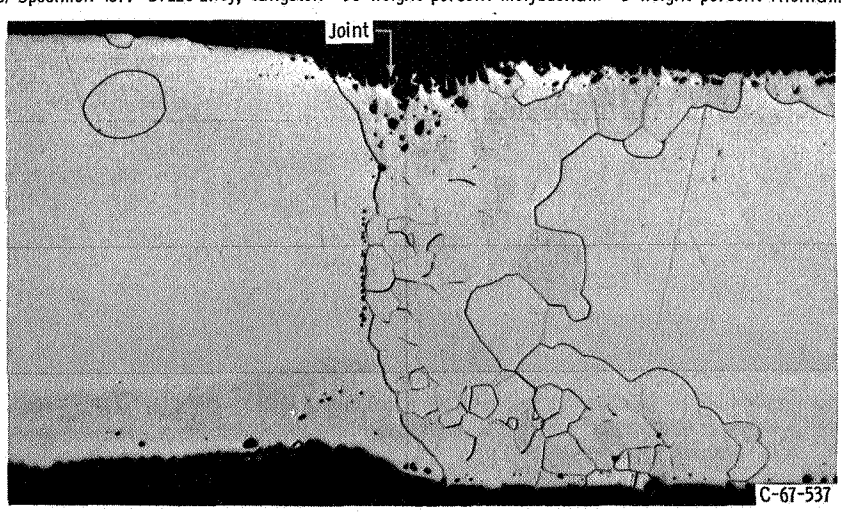
Figure 9. - Mode of fracture in tungsten base metal of specimen 385 brazed with tungsten - 25-weight-percent-osmium (joint region not shown). Note relatively fine-grained tungsten base metal at left and single grain in region of high reduction in area. Etchant, Murakami's reagent. X50. (Reduced 30 percent in printing.)



(a) Specimen 395. Braze alloy, tungsten - 25-weight-percent osmium.



(b) Specimen 407. Braze alloy, tungsten - 50-weight-percent-molybdenum - 3-weight-percent-rhenium.



(c) Specimen 398. Braze alloy, molybdenum - 5-weight-percent-osmium.

Figure 10. - Cross sections of brazed joints (taken from cutouts) after heat treatment in hydrogen for 10 hours at 2500° C. Porosity and loss of material at surface is evident in molybdenum-bearing braze metals. Etchant, Murakami's reagent. X100.

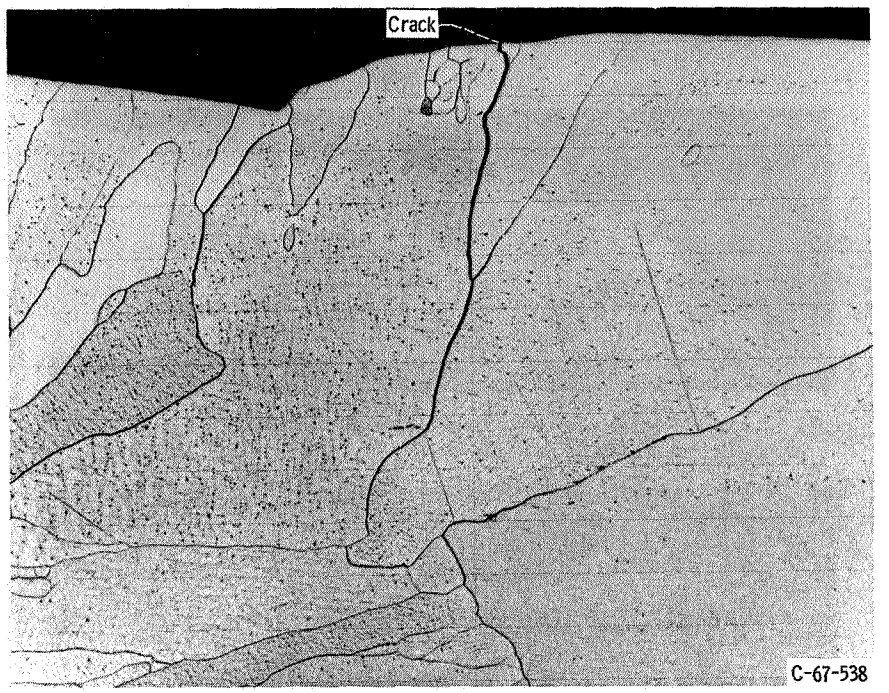


Figure 11. - Longitudinal section showing intergranular hot cracking in single-phase, tungsten - 50-weight-percent-molybdenum - 3-weight-percent-rhenium braze metal. Etchant, Murakami's reagent. X100.

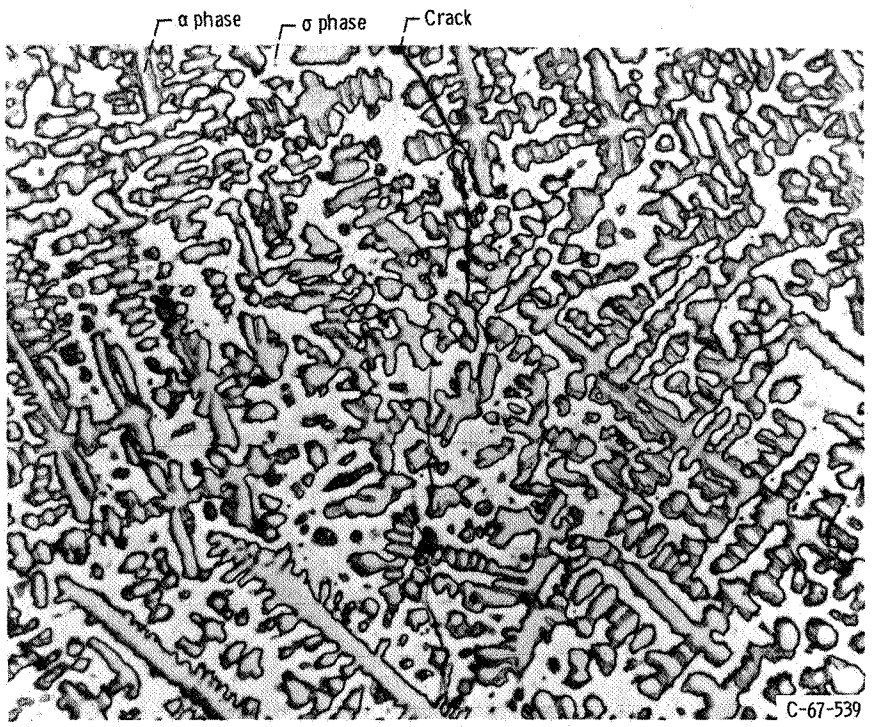
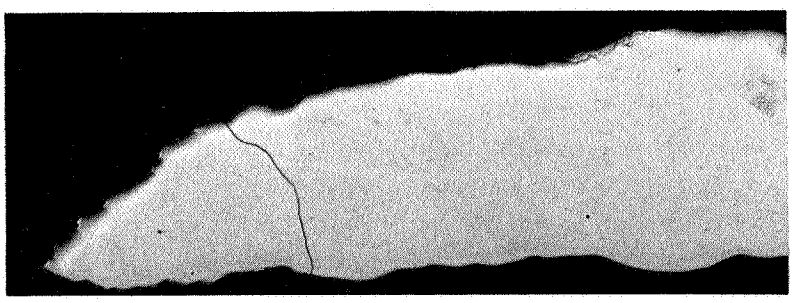
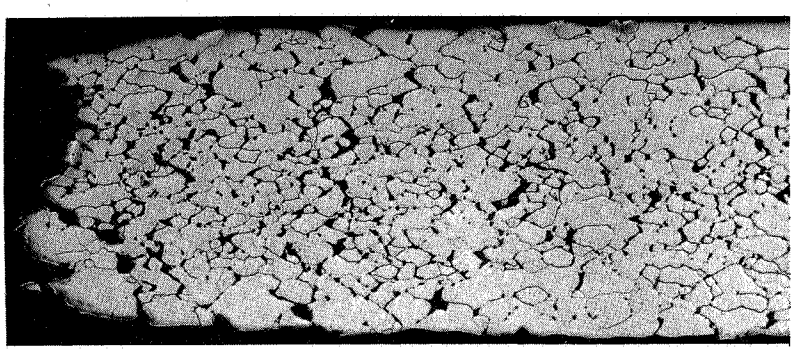


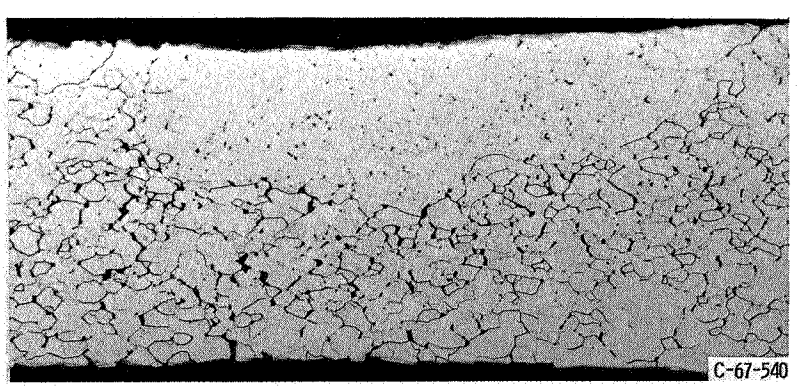
Figure 12. - Longitudinal section showing cold-cracking problem in tungsten - 25-weight-percent-osmium braze metal in as-brazed condition. Note that this cracking avoids tungsten-rich α phase and tends to follow σ phase. Etchant, Murakami's reagent. X500.



(a) Cross section of fracture surface in weakest specimen. Ultimate tensile strength, 2820 pounds per square inch.



(b) Cross section of fracture surface in strongest specimen. Ultimate tensile strength, 5080 pounds per square inch.



(c) Cross section of strongest specimen somewhat removed from fracture surface. Ultimate tensile strength, 5080 pounds per square inch.

Figure 13. - Microstructures of as-received, tungsten base-metal specimens after tensile testing at 2200° C in vacuum. Etchant, Murakami's reagent. X100.

NASA-Langley, 1967 —— 17 E-3634

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